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(54) LASER IMAGABLE DRY PLANOGRAPHIC PRINTING PLATE BLANK

(71) We, SCOTT PAPER COMPANY, a Corporation organized and existing under the laws of the State of Pennsylvania, United States of America, of Industrial Highway at Tinicum Island Road, Delaware, County, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to dry planographic printing plate blanks.

Dry planographic printing plates are disclosed in United States Patent 3,677,178. Such plates comprise a flexible substrate having coated therein a cured solid but elastic silicone rubber film which will not remove conventional lithographic ink from an ink roller on a printing press.

Recently, methods have been proposed to utilize a laser beam to image a planographic (offset) or raised-image (letter press) printing plate, see for example United States Patent Nos. 3,506,779 "Laser Beam Type Setter" and 3,664,737 "Printing Plate Recording by Direct Exposure". While the laser beam offers great promise in producing high resolution printing plates, there has thus far been no practical way to image a dry planographic printing plate. The silicone rubber which repels printing ink, is unaffected by laser radiation. The silicone rubber layer appears to be transparent to the laser beam energy and no significant reaction takes place. It might be possible to directly image a photosensitive dry planographic plate with a laser beam which emits light in the ultraviolet region. The disadvantage of such lasers is, however, that they are presently very expensive and do not have a high power output. In addition, such photosensitive plates would have to behandled under special, non-active lighting as overall exposure to ultraviolet would destroy their imaging capability. Furthermore, the shelf-life of any photosensitive coating is limited.

It is therefore of interest to provide a dry planographic printing plate which can be imaged by the use of a laser in a practical, commercially feasible manner.

According to this invention there is provided a dry planographic printing plate blank comprising, on an ink receptive substrate;

a laser responsive layer which contains particles which absorb laser energy, a binder which oxidizes under the influence of laser radiation and a cross-linkable resin together with a cross-linking agent; and

a film of ink repellent silicone rubber overlying and in adherent contact with said layer.

With reference to the accompanying drawing:

Figure 1 is a cross-sectional view showing the construction of the dry planographic printing plate blank of the present invention;

Figure 2 is a cross-sectional view illustrating the formation of an image on the blank of the present invention to provide a printing plate.

In a preferred embodiment these laser energy absorbing particles are carbon particles and the oxidizable binder is nitrocellulose. The cross-linkable resin is preferably cross-linked by means of a cross-linking agent. As will be more fully illustrated hereinafter, the cross-linking reaction is conveniently initiated by heat. An image is recorded on the plate by writing with a laser beam in a conventional manner.

The laser-responsive coating utilized in the present invention absorbs radiation in the

infrared as well as the visible range. A suitable beam may be applied by YAG (yttrium-aluminum-garnet) laser which has an effective wave length of about 1.06 microns or by an argon laser beam which has an effective wave length in the range of from 0.48 to 0.52 micron. The beam of radiant energy is applied to the laser-responsive coating to loosen or vaporize and remove it and the overlying silicone rubber in selected areas so as to expose the underlying substrate.

In the areas irradiated by the laser beam the laser responsive layer and the silicone rubber are removed, exposing the underlying lithographic substrate. The plate then accepts ink in the area struck by laser beam and repels ink in the non-image areas, as these areas are constituted by silicone rubber. The thus-imaged plate is subjected to an appropriate treatment, such as heating, to cross-link the resin in the remaining portions of the laser responsive layer, thereby forming a firm bond between the silicone rubber film and the underlying substrate and providing durable background areas on the planographic printing plate.

Referring now to the drawings, Fig. 1 depicts the composite structure of the dry planographic printing plate blank of the present invention. Substrate 10 may be a sheet of material conventionally used as a support for offset duplicating plates, e.g., metal, especially aluminum, paper or plastics. If such material is not itself ink-receptive, it must be provided with an oleophilic or ink-receptive surface layer. In the embodiment illustrated, the substrate 10 is aluminum. Since metals such as aluminum are so highly conductive of heat, in order to prevent the metal from dissipating the thermal energy provided by the laser, the substrate 10 is provided with a layer 11 of an olephilic or ink receptive resin which is also heat insulating.

The composition of the resin for layer 11 is not critical; any of the oleophilic resins which are commonly used in the lithographic printing art and which provide good adhesion to the metal are suitable and the choice of such a resin is well within the skill of the worker in the art. Illustrative of the ink receptive resins suitable for use in the present invention include phenol- and cresol-formaldehyde resins especially the Novolak resins, urea-formaldehyde resins, melamine-formaldehyde resins, vinyl resins, alkyd resins, polyester resins, polyacrylate including polymethacrylate and polyethylacrylate resins, polyamides (nylon), polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polystyrene, copolymers of styrene and butadiene and polyalkylene especially polyethylene. Insulating layer 11 may be applied to the substrate 10 by conventional coating techniques in the form of an aqueous latex or organic solvent solution. Alternatively, the resin may be applied by extruding it in the molten form, a technique commonly referred to as "hot melt" extrusion. In some cases, a film of a resin such as polyethylene, polystyrene or polyvinyl acetate may be laminated to substrate 10.

Over the insulating layer 11 is applied a laser-responsive layer 12 which comprises particles which absorb layer energy, such as carbon black, a binder which oxidizes under the influence of laser radiation, such as nitrocellulose and a cross-linkable resin, such as a "novolak" resin in combination with a cross-linking agent. Over the laser-responsive layer 12 is applied a silicone rubber top coating 13. Not illustrated, but preferred to insure good adhesion between the laser-responsive layer and the silicone rubber top coating 13, is the application of a primer for silicone rubber such as polytetrabutyl titanate or polytetraisopropyl titanate.

When the laser-responsive layer 12 is struck by appropriate laser radiation, it oxidizes or burns. The products of combustion from the irradiated area of the laser responsive layer 12, being hot and at least partially gaseous, necessarily attempt to escape their confinement between layers 13 and 11. The result, as shown in Fig. 2, is that the silicone rubber overlying the irradiated area is either directly removed by the escaping products of combustion or the bond of the silicone rubber to the underlying layers is sufficiently weakened that it can later be removed by the application of a suitable developer solution.

After development, the imaged plate is subjected to a heat treatment of, for example, 400°F., for one-half minute, to initiate the cross-linking reaction in the cross-linkable resin to increase the adhesion of the silicone rubber remaining in the background areas, thus increasing run length of the plate.

EXAMPLE I

To a 3 mil. thick sheet of Mylar RTM polyester film was applied a laser responsive coating of the following composition:

	Parts by Weight
Carbon black	15.4
Nitrocellulose (self-oxidizing)	7.7
"novolak" resin (non-oxidizing cross-linkable resin)	60.9
Melamine derivative cross-linking agent ("Cymel" RTM 301 sold by American Cyanamid Co.)	15.4
p-toluene sulfonic acid (catalyst)	0.6

Methyl ethyl ketone in an amount sufficient to adjust total solids content to 20% by weight.

The coating composition was applied to the substrate using a No. 6 mayer rod and dried. The weight of the dry coating was 0.5 pounds per ream, (3,300 square feet).

Over this laser-responsive coating was applied a tie coat of polytetrabutyl titanate (DuPont "Tyzor" PB) to enhance adhesion between the laser responsive coating and the subsequently applied silicone rubber. The tie coat was applied as a 4% organic solvent solution by a No. 6 Mayer bar in a nominal amount of less than 0.1 pounds per ream (dry weight basis). Thereupon, a layer of silicon rubber ("Dow Corning 79-037 RTV" RTM) was applied by No. 16 Mayer rod in an amount of 3 pounds per ream (dry weight basis).

An image was etched into the plate by means of a YAG laser beam. The plate was developed by application of naphtha solvent to remove debris in the irradiated areas, leaving the polyester substrate exposed in the image areas.

After heating to effect cross-linking of the cross-linkable resin the developed plate was mounted on an offset duplicating press without connecting the dampening system and yielded many satisfactory copies.

EXAMPLE II

To a 5 mil. thick sheet of aluminum provided with a coating of a cross-linked carboxy polyvinyl benzal (disclosed in United States Patent 3,776,888) was applied a laser responsive coating of the following composition:

	Parts by Weight
Carbon black	10
Nitrocellulose	5
"novolak" resin (non-oxidizing)	50
Melamine derivative cross-linking agent ("Cymel" RTM 301 sold by American Cyanamid Co.)	2.5
p-toluene sulfonic acid	0.1

Methyl ethyl ketone in an amount sufficient to adjust total solids content of 20% by weight.

The coating composition was applied to the substrate using a No. 4 mayer rod and dried. The weight of the dry coating was 0.65 pounds per ream, (3,300 square feet).

Over this laser-responsive coating was applied a tie coat of polytetrabutyl titanate (DuPont "Tyzor" PB) to enhance adhesion between the laser-responsive coating and the subsequently applied silicone rubber. A tie coat was applied as a 4% organic solvent solution by a No. 5 Mayer bar in a nominal amount of less than 0.1 pounds per ream (dry weight basis). Thereupon, a layer of silicone rubber ("Dow Corning 79-037 RTV") was applied by No. 16 Mayer rod in an amount of 3 pounds per ream (dry weight basis).

An image was etched into the plate blank by means of a YAG laser beam. The plate was developed by application of naphtha solvent to remove debris in the irradiated areas, leaving the coated aluminum substrate exposed in the image areas.

After heating to effect cross linking of the cross-linkable resin the developed plate was mounted on an offset duplicating press without connecting the damping system and yielded many satisfactory copies.

While the invention has been particularly described with reference to preferred embodiments thereof, it is understood that various other changes and modifications thereof will occur to a person skilled in the art without departing from the scope of the invention as defined by the appended claims.

WHAT WE CLAIM IS:—

1. A dry planographic printing plate blank comprising, on an ink receptive substrate:

a laser-responsive layer which contains particles which absorb laser energy, a binder which oxidizes under the influence of laser radiation and a cross-linkable resin together with a cross-linking agent; and

a film of ink-repellent silicone rubber overlying and in adherent contact with said layer.

2. A plate according to claim 1, wherein the substrate is metal provided with a heat insulating layer of an ink receptive resin.

3. A plate according to claim 1 or 2, wherein the particles are carbon black.

4. A plate according to any one of claims 1 to 3, wherein the self-oxidizing binder is nitrocellulose.

5. A dry planographic printing plate blank substantially as hereinbefore described with reference to the Examples and/or Fig. 1 of the accompanying drawing.

6. A method of making an imaged dry planographic printing plate comprising the steps of:

a) directing laser radiation onto the laser-responsive layer of a blank according to any of claims 1 to 5 so as to selectively loosen or vaporize the exposed areas of the laser-responsive layer and the overlying areas of the silicone rubber film to define an image on the blank;

b) removing any remaining loosened areas to provide a developed blank; and

c) treating the developed blank to effect cross-linking of said cross-linkable resin.

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1489308 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

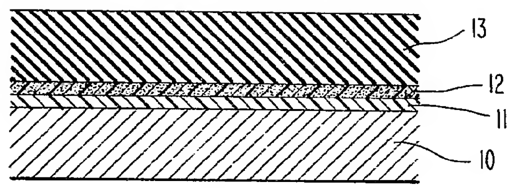

Fig. 1

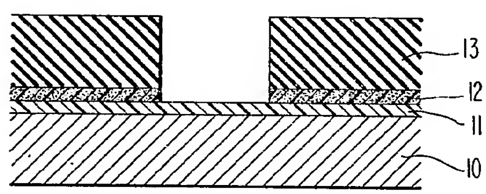

Fig. 2